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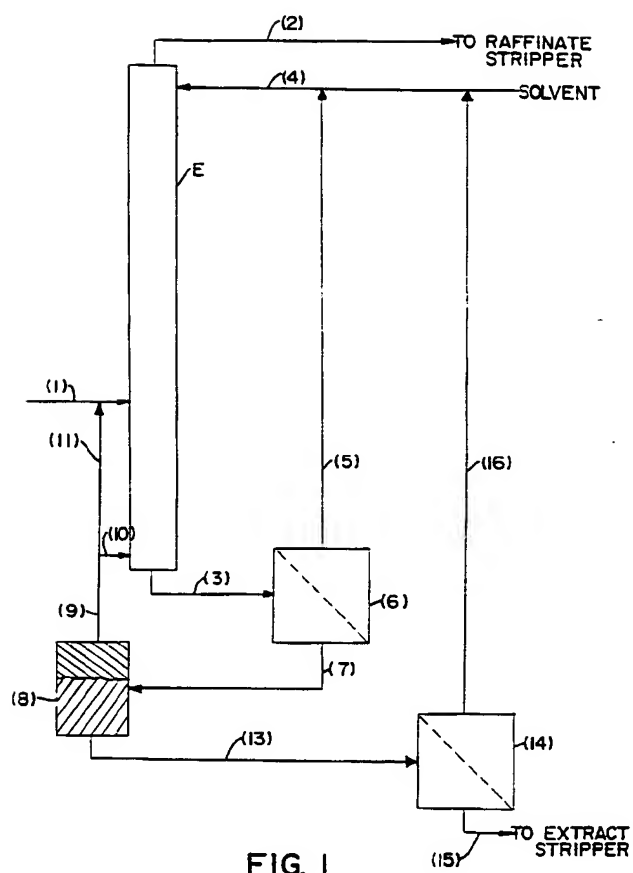
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(54) **Solvent extraction process involving membrane separation of extract phase and/or intermediate zone phase with pseudo extract/pseudo raffinate recycle.**

(57) The solvent extraction of aromatics containing oil using a selective aromatics extraction solvent to produce an aromatics rich extract phase and an oil rich/aromatics lean raffinate is improved by the steps of subjecting the extract phase to a membrane separation step to produce a permeate phase and a retentate phase passing the retentate phase to a settling zone wherein the retentate phase spontaneously separates into two liquid phases, and recycling the upper phase to the extraction zone, either to the feed inlet or to the bottom of the extract reflux zone to thereby increase the raffinate oil recovered from the extraction tower.

Alternatively or in addition to the above, a side stream can be taken from an intermediate zone of the extraction zone (e.g. extraction tower) and fed to a membrane separation to produce a solvent rich permeate and an oil rich retentate. The solvent rich permeate is recycled while the oil rich retentate is fed to a settling zone wherein it will spontaneously separate into an oil rich pseudo raffinate upper phase which is recovered and into a solvent rich pseudo extract bottoms phase which is recycled to the solvent extraction zone, preferably at a point below that at which the side stream was withdrawn.

The membrane separation zone preferably employs interfacially polymerized membranes under reverse osmosis conditions.



Brief Description of the Invention

The solvent extraction of aromatics containing oil using a selective aromatics extraction solvent to produce an aromatics rich extract phase and an oil rich/aromatics lean raffinate is improved by the steps of  
 5   subjecting the extract phase preferably containing from about 5 to about 25% oil, more preferably containing about 10 to about 18% oil to a membrane separation step to produce a permeate phase and a retentate phase and passing the retentate phase to a settling zone such as a settling drum wherein the retentate phase spontaneously separates into two liquid phases. The upper phase, containing good quality lubricating oil molecules can be recycled to the extraction zone, either to the feed inlet or to the bottom of  
 10   the extract reflux zone to thereby increase the raffinate oil recovered from the extraction tower.

Alternatively or in addition to the above a side stream can be taken from an intermediate zone of the extraction zone (e.g. extraction tower) and fed to a membrane separation unit wherein the mixed extract solution/raffinate solution feed stream taken from the intermediate zone of the extraction zone is fed to a membrane separation zone to produce a solvent rich permeate and an oil rich retentate. The solvent rich  
 15   permeate is recycled while the oil rich retentate is fed to a settling zone wherein the oil rich retentate will spontaneously separate into an oil rich pseudo raffinate upper phase which is recovered and into a solvent rich pseudo extract bottoms phase which is recycled to the solvent extraction zone, preferably at a point below that at which the side stream was withdrawn.

20   Background of the Invention

French patent 2,595,370 teaches a multiple effect extraction process using counter current solvent flow. The process utilizes a main column separated into 2 zones by a draw off tray and a second column which fractionates the side stream drawn off from the first column. The fractionation zone produces an over head  
 25   raffinate which is fed back to the top zone of column 1 above the draw-off tray. The bottoms from the fractionation zone are cooled and separate into a pseudo raffinate and an extract. This extract is recycled to the bottom zone of column 1 just below the draw-off tray. It can optionally also be fed into the top zone of column 1 just above the draw-off tray. By this scheme a raffinate is recovered from the top of the first column, an extract from the bottom of said column and a pseudo raffinate from the separation zone to  
 30   which the bottoms fraction from the fractionation zone is fed.

In an alternate embodiment the extract from the bottom of column 1 can be cooled to salt-out in a separation zone an upper phase of lighter hydrocarbons which is recycled back to the bottom of the bottom zone of column 1. The bottoms fraction from this separation zone is a true extract phase.

French Patent 2,595,371 teaches a process for the selective solvent extraction of a hydrocarbon  
 35   mixture. Solvent is passed counter currently to the hydrocarbon feed employing 2 or more separation columns resulting in the separation of the feed into a raffinate, a pseudo-raffinate and an extract. Feed is introduced into a first column while fresh solvent is introduced into the top of a second column. The overheads from the first column constitute the feed to the second column. The bottoms from the second column are cooled and permitted to salt-out in a separation zone wherein an upper phase pseudo raffinate  
 40   is recovered and a bottom phase of recycle solvent is recovered. This bottom phase recycle solvent is used as the solvent introduced into the first column. Extract is recovered from the bottom of the first column and raffinate from the top of the second column. In an alternative embodiment part of the pseudo raffinate can be cycled back to the bottom of the second column while the extract from the first column can be cooled to salt-out in a separation zone producing a upper phase of lighter hydrocarbon which is recycled to the  
 45   bottom of the first column, and a true extract bottoms phase.

U.S. Patent 4,311,583 teaches a solvent extraction process. A hydrocarbon feed is contacted with N-methyl pyrrolidone in an extraction zone. The primary extract is separated into a secondary raffinate and a secondary extract by cooling the primary extract optionally with the addition of water or wet solvent. The secondary raffinate is separated from the secondary extract. At least part of the secondary raffinate is  
 50   combined with the primary raffinate to obtain an increased yield of desired quality raffinate oil product. A part of the secondary raffinate may be returned to the lower part of the extraction zone.

U.S. Patent 4,328,092 teaches the solvent extraction of hydrocarbon oils. The process uses N-methyl-2-pyrrolidone. The extract from the solvent extraction zone is cooled to form two immiscible liquid phases, a secondary extract phase and a secondary raffinate phase. The secondary raffinate phase is recycled to the  
 55   extraction zone resulting in increased yield of refined oil product and in energy savings.

"Liquid Extraction" 2d Ed, R. E. Treybol, McGraw-Hill Book Company, 1963 pgs 144-145, 270-273. This reference shows that extractor reflux has been practiced and that reflux for extraction operations is obtained by distillation methods, chilling or by the addition of an anti solvent.

## Description of the Figures

Figure 1 presents a schematic of the present invention practiced on the extract phase with recycle of the upper phase from the settling zone to the extraction zone.

Figure 2 presents a schematic of the present invention practiced on both an intermediate zone side stream and on the extract phase.

## The Present Invention

The solvent extraction of aromatics containing oil using a selective aromatics extraction solvent to produce an aromatics rich extract phase and an oil rich/aromatics lean raffinate is improved by the steps of subjecting the extract phase preferably containing from about 5 to about 25% oil, more preferably containing from about 10 to about 18% oil to a membrane separation step to produce a permeate phase and a retentate phase and passing the retentate phase to a settling zone such as a settling drum wherein the retentate phase spontaneously separates into two liquid phases. The upper phase, containing good quality lubricating oil molecules can be recycled to the extraction zone, either to the feed inlet or to the bottom of the extract reflux zone to thereby increase the raffinate oil recovered from the extraction tower.

Alternatively or in addition to the above a side stream can be taken from an intermediate zone of the extraction zone (e.g. extraction tower) and fed to a membrane separation unit wherein the mixed extract solution/raffinate solution feed stream taken from the intermediate zone of the extraction zone is fed to a membrane separation zone to produce a solvent rich permeate and an oil rich retentate. The solvent rich permeate is recycled while the oil rich retentate is fed to a settling zone wherein the oil rich retentate will spontaneously separate into an oil rich pseudo raffinate upper phase which is recovered and into a solvent rich pseudo extract bottoms phase which is recycled to the solvent extraction zone, preferably at a point below that at which the side stream was withdrawn.

Treating a raffinate or a sidestream withdrawn from a separation tower to separate it into a pseudo raffinate and a pseudo extract by means of distillation followed by settling or by anti solvent addition and/or cooling followed by settling have been described on the literature as recited above. All of these techniques, as well as the present invention rely on introducing a change in conditions on the solution being treated so that the solution will spontaneously separate into a pseudo raffinate and a pseudo extract. However, the conventional methods of distillation, cooling or anti-solvent addition have drawbacks such that they are not actually practical to use. For example, cooling of extract solution will generate only little raffinate, limiting the yield of product to less than 20% on feed. In addition; the pseudo extract solution has to be reheated substantially before recycling to the tower.

Water addition can produce adequate yield of product, but has to be removed from the pseudo extract solution before it can be reused, and is therefore impractical. In addition, addition of water results in a loss of selectivity.

Distillation could remove part of the solvent, similar to the membrane unit, but requires a substantial amount of equipment, plus a large temperature increase to reach the solvent boiling point, followed by an equally large temperature decrease before the settling drum. Consequently partial solvent recovery using distillation has always proven to be impractical.

The process of the present invention overcomes these disadvantages. Furthermore, use of membrane separation on the sidestream has additional benefits compared even to membrane solvent recovery on the extract. Feed contamination, e.g. Iron sulfide or other particulate matter is less likely to reach the membrane, and fouling should be less of a problem, and the extract oil at the sidestream location is less aromatic than the conventional extract, consequently, less oil will permeate, and any oil that may permeate has less effect on solvent quality and on its subsequent use at the tower top.

The membrane separation zone for the separation of solvent from the extract phase, raffinate phase or intermediate phase may employ regenerated cellulose membrane under reverse osmosis conditions as taught in US Patent 4,510,047 or, preferably the interfacially polymerized membranes disclosed and claimed in copending application USSN 417,333 filed October 5, 1989 in the name of Laura E. Black.

The present invention preferably uses interfacially polymerized membranes on a solvent resistant backing, for the separation of the aromatic extraction solvents such as N-methyl pyrrolidone (NMP), phenol, sulfolane, furfural, N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and dimethyl-acetamide (DMAc), preferably NMP, phenol or furfural from oil. The solvent resistant backing is an ultrafiltration membrane with pore sizes in the range of 0.02 to 0.1 microns and is composed of generally insoluble polymers such as nylon 6,6, cellulose, polyester, teflon, polypropylene and other insoluble polymers,

preferably nylon 6,6. These membranes provide much higher fluxes and oil rejections in the separation of extraction solvents from oil than do commercially available regenerated cellulose membranes (see U.S. Patent 4,510,047).

The interfacially polymerized membranes are prepared by reacting multifunctional amino reactants dissolved in water with other polyfunctional agent reactants dissolved in organic solvents. The interfacially polymerized membrane is produced on a non-selective, microporous ultrafiltration support layer which is inert in the organic media to which it will be exposed. This support layer is selected from nylon, cellulose, polyester, teflon, polypropylene, polyethylene terephthalate etc. ultrafiltration membranes having pores in the range 0.02 $\mu$  to 0.1 $\mu$ .

A few examples of multi-functional amino group reactants include polyethylenimine, polyvinylamine, polyvinylanilines, polybenzylamines, polyvinylimidazolines, amine modified polyepihalohydrins, and other amine containing polymers, m-phenylene diamine, p-phenylene diamine, triaminobenzene, piperazine, piperidine, 2,4-bis (p-aminobenzyl) aniline, cyclohexane diamine, cycloheptane diamine, etc. and mixtures thereof.

The polyfunctional agents that the amines are reacted with can include di- and tri- acid halides, e.g. chlorides, acid anhydrides, aliphatic and aromatic diisocyanates, thioisocyanates, haloformates (e.g. chloroformates) and sulfonyl halides, (e.g. sulfonyl chlorides), and mixtures thereof. A few examples of these agents are trimesoyl chloride, cyclohexane-1,3,5 tricarboxyl chloride, isophthaloyl chloride, terephthaloyl chloride, diisocyanatohexane, cyanuric chloride, diphenylether disulfonyl chloride, formyl chloride, acetyl chloride, propionyl chloride, butyryl chloride, valeryl chloride, caproyl chloride, heptanoyl chloride, valeryl chloride, caproyl chloride, heptanoyl chloride, octanoyl chloride, pelargonyl chloride, capryl chloride, lauryl chloride, myristyl chloride, palmityl chloride, margaryl chloride, stearyl chloride etc., oxalyl chloride, malonyl chloride, succinyl chloride, glutaryl chloride, fumaryl chloride, glutaconyl chloride, acetic anhydride, propionic anhydride, butyric anhydride, phthalic anhydride, ethylene diisocyanate, propylene diisocyanate, benzene diisocyanate, toluene diisocyanate, naphthalene diisocyanate, methylene bis (4-phenylisocyanate), ethylene thioisocyanate, toluene thioisocyanate, naphthalene thioisocyanate, ethylene bischloroformate, propylene bischloroformate, butylene bischloroformate, 1,3-benzenedisulfonyl chloride, 1,4 benzene disulfonyl chloride, 1,3-naphthalene disulfonyl chloride and 1,4-naphthalenedisulfonyl chloride, etc. and mixtures thereof.

A crosslinked membrane is used in the present invention to ensure stability in the organic solutions. A crosslinked polymeric film is formed if these membranes are prepared with one of the reagents being at least trifunctional. The degree of crosslinking is primarily controlled by the concentration of the reactant solution with higher concentrations leading to higher degrees of crosslinking. Membranes prepared from high concentration solutions generally show higher solute rejections when tested under reverse osmosis conditions.

In general the interfacially polymerized membranes are produced using 0.1 to 10 wt% aqueous solutions of the amines, preferably 0.25 to 5 wt% aqueous solutions of the amines; and 0.1 to 5 wt% non-aqueous solutions of the poly-functional agents, preferably 0.15 to 0.5 wt% non-aqueous solution of the poly-functional agent.

Following the sequential deposition of the two solutions, the resulting film can be heated to promote crosslinking of any unreacted amine. This post heating step can be at a temperature of about 60 to 150 °C, preferably 80 to 120 °C for from 1 to 20 minutes. The concentrations of components used and drying/crosslinking times and temperatures selected from the above ranges will be selected by the practitioner in response to the membrane casting procedures actually employed and the casting machines or other mechanisms or equipment used.

The selective aromatics extraction solvents such as N-methyl-2-pyrrolidone (NMP), phenol, furfural, N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and dimethylacetamide (DMAC) used to extract aromatic hydrocarbons from hydrocarbon oils such as specialty oils or white oils are themselves recovered from the raffinate phase, extract phase or both resulting from such extraction by permeation under reverse osmosis conditions through the interfacially polymerized membranes. Reverse osmosis conditions include contacting the thin, interfacially polymerized crosslinked face of the membrane with the raffinate phase, extract phase, or both, preferably extract phase at a temperature between about -24 to 200 °C, preferably 40 to 150 °C and under an applied pressure sufficient to overcome the osmotic pressure. Pressures on the order of 0 to 1000 psig can be used, preferably about 400 to 600 psig.

The aromatic extraction solvent recovered as permeate may be recycled to the beginning of the extraction process or introduced into the extraction zone somewhat downstream of the fresh solvent inlet at a point where the composition of the membrane recovered solvent matches the composition of the solvent/oil mixtures in the extraction zone.

In the case of the extraction of lubricating oil stocks, the retentate recovered from the membrane separation of the extract phase from the extraction tower is a concentrated extract solution which will spontaneously separate into two liquid phases when the retentate is allowed to settle in for example, a settling zone such as a settling drum. The upper phase from the settling drum will contain good quality lubricating oil molecules which can be recycled to the extraction tower, either to the feed inlet or to the bottom of the extract reflux zone in the extraction tower. This will increase the yield of raffinate oil recovered from the extraction tower. The bottom phase recovered from the settling drum can be further treated with membranes for additional solvent recovery or can be sent to conventional solvent recovery equipment with the recovered extract being sent on for conventional processing.

Alternatively or in addition to the above, a side stream can be taken from an intermediate zone of the extraction tower and fed to a membrane separation unit wherein the mixed raffinate solution/extract solution feed is separated into a raffinate rich permeate and an extract rich retentate according to the procedure of USSN 434,735 filed November 1989 in the name of James R. Sweet, now US Patent 4,978,454.

According to the present invention the retentate oil rich phase is sent to a settling zone such as a settling drum to spontaneously separate into an oil rich pseudo raffinate upper phase which is recovered and into a solvent rich pseudo extract bottoms phase which is recycled to the solvent extraction tower preferably at a point below that at which the side stream was withdrawn.

Referring to the figures it is seen in Figure 1 that hydrocarbon oil feed is fed via line 1 to the extraction zone (E). Solvent is fed via line 4 into extraction zone E and passed countercurrently to the hydrocarbon oil feed. An aromatics lean/oil rich raffinate stream is recovered via line 2 and sent to the raffinate stripper (not shown) for further processing. An aromatics rich extract phase is recovered via line 3 and fed to a membrane separation zone (6) wherein a solvent rich permeate is recovered and recycled via line 5 to line (4) for re-introduction to the extraction zone E. A retentate phase is recovered via line 7 and passed to settling zone (8) wherein it spontaneously separates into two liquid phases. The upper phase containing good quality lube oil molecules is recycled via line 9 back to extraction zone E and fed into extraction zone E via either line 10 at the bottom of the zone or via line 11 back to the feed inlet line 1. The bottoms layer from settler 8 may be fed via line 13 to membrane separation unit 14 wherein a solvent rich permeate is recovered via line 16 and recycled to line 4 for re-introduction to extraction zone E. The retentate is recovered via line 15 and sent to the extract stripper, not shown, for further processing. Alternatively, the bottoms phase from settler 8 may be sent via a bypass line (not shown) directly to the extract stripper (not shown) for further processing.

Figure 2 is a variant of the present novel process. Hydrocarbon feed is introduced via line (1) into extraction zone (2). Fresh and/or recycled solvent is fed into extraction zone (2) via line (3). The solvent and hydrocarbon feed are countercurrently contacted in zone (2). An intermediate extraction solution stream is withdrawn from zone (2) via line (6) and fed to membrane separation zone (M1) wherein a solvent rich permeate stream is recovered via line (7) and recycled to zone (2) via line (3). A retentate phase is recovered via line (8) and fed to a settling zone (9) wherein it spontaneously separates into two liquid phases, a pseudo raffinate recovered via line (10) and a pseudo extract recovered via line (11) and fed via line (12) back to the extraction zone (2) at a point somewhat lower than that at which the intermediate zone side stream was withdrawn. An extract phase is recovered from zone (2) via line (5) and fed to membrane separation zone (M2) wherein a solvent rich permeate is recovered via line (13) and recycled to lines (11) and (12) for re-introduction into the extraction zone (2). A retentate is recovered via line (14) and fed to a settling zone 15 wherein the retentate spontaneously separates into two liquid phases. The upper phase containing good quality oil molecules is recycled via line 16 to line 1 for introduction as feed back into extraction zone 2. The bottoms phase recovered via line 17 can be separated into solvent and extract in a membrane zone or other separation zone (not shown) for appropriate disposition.

## Experimental

### Example 1

A 50 wt% water solution of polyethylenimine was used as supplied from Aldrich (Aldrich cat # 18,197-8). A sample of diphenyl methane -4,4 diisocyanate (also referred to as methylene diisocyanate or MDI) was used as received from BASF Wyandotte Corporation. Ultipor nylon 66 membranes with 0.1 $\mu$  pore size were used as supplied by Pall Ultrafine Filtration Corporation.

The polyethylenimine (PEI) was further diluted with deionized water to prepare several solutions with various PEI concentrations ranging from 0.35 to 2.6 wt%. A toluene/hexane solution containing approximately 0.4 wt% MDI was prepared. Several membranes were prepared using the following procedure.

A disc of the nylon 6,6 membrane support was installed in a wash coat cell where one side of the membrane was left exposed. A polyethylenimine solution was poured over the exposed side of the membrane and was allowed to remain for 1 minute. The excess solution was then drained off the membrane for 1 minute. The MDI solution was then poured over the exposed side of the membrane and was allowed to remain for 1 minute and was then drained for 1 minute. The membrane was then placed in an oven (at temperatures  $>100^{\circ}\text{C}$ ) for 10 minutes. After this heat treatment, the resulting interfacially polymerized, crosslinked polyurea membrane was ready for testing.

The membrane performance was tested by circulating a sample of an extract oil solution (average molecule weight of oil = 400 g/mole) containing 12 vol % oil in NMP over the thin interfacially polymerized crosslinked face of the membranes at  $70^{\circ}\text{C}$  and at an applied feed pressure of 500 PSIG. The permeate yield was kept below 5% to ensure that the feed composition did not change during testing. The membranes were tested for 2 to 3 hours, during which time the membrane flux was recorded and permeate samples collected. The membranes were then left in the test unit overnight in the extract solution at ambient temperatures with no applied feed pressure. The next morning, the membranes were retested for an additional 2 to 3 hours with additional permeate samples being collected. The volume percent oil in both the feed and the permeate samples were measured.

The interfacially polymerized membranes had fluxes ranging from about 200 to  $750\text{ l/m}^2\text{day}$  with corresponding oil rejections of  $>98\text{ vol}\%$  to  $88\text{ vol}\%$  (Table 1). Both the concentration of the polyethylenimine in the water wash solution and the heat treatment temperature affected the membrane performance. The high oil rejection of  $>98\%$  was obtained with the highest PEI concentration tested of 2.63%.

**TABLE 1**  
**EQUILIBRIUM PERFORMANCE OF INTERFACIALLY**  
**POLYMERIZED MEMBRANES**

Temperature = 70°C  
 Pressure = 500 psi  
 Feed = 12 vol% 150N extract oil/NMP  
 Membrane : prepared by reacting aqueous solution of  
 polyethylenimine with 0.4 wt% methylene  
 diisocyanate in toluene/hexane on a 0.1  
 nylon 6,6 ultrafiltration membrane

Run No.	wt% PEI In Water	Heat Treatment Temperature °C	Flux $l/m^2 \cdot day$	Oil Rejection(1) %
A	2.63	135	210	>98
B	2.63	145	196	>98
C	0.67	145	750	88
D	0.67	112	330	94
E	0.35	112	477	96

\* performance at end of the second test period after the membranes had soaked in the feed solution overnight

(1) oil rejection accurate to  $\pm 1.5$  vol%

After the overnight soak period, the flux exhibited by the membranes increased by about 50  $l/m^2 \cdot day$ . The reason for this increase is not understood. The membrane rejection stayed essentially the same or increased in a couple of cases. The long term stability of these membranes in NMP solutions is not yet known.

#### Example 2

Membranes were prepared in a continuous manner on an interfacial polymerization machine using nylon 6,6 membrane with 0.04 $\mu$  pore size obtained from Pall Ultrafine Filtration Corporation as support. Solutions were prepared of 1,4-phenylene diamine in water and 0.14% trimesoyl chloride in Chevron 250B.

The web speed on the IFP machine was adjusted so that the contact time in the amine solution was 50 seconds, the in-between evaporation period was 10 minutes and 25 seconds, and the contact time in the trimesoyl chloride solution was 45 seconds. Backside wetting of the nylon membrane in the amine solution



plus the longer contact time ensured that the nylon membrane was saturated with the amine solution and that adequate reaction occurred in the trimesoyl chloride bath. Membranes were prepared with varying amine concentrations and were reacted with a 0.25% trimesoyl chloride solution.

Membrane performance was determined by circulating a sample of an extract oil solution (average molecular weight of oil = 400 g/mole) containing 14 vol% oil in NMP over the membrane at 70°C at an applied feed pressure of 500 PSIG. The permeate yield was kept below 5% to ensure that the feed composition did not change during testing. The membrane flux was recorded and permeate samples collected. The volume percent oil in both the feed and permeate samples was measured.

Membrane	% 1,4-PDA	Flux l/m <sup>2</sup> day	Oil Rejection vol%
G	2.0	350	96
H	2.0	315	96
I	1.2	340	96
J	0.6	400	92
K	0.3	325	88

Down to an amine concentration of 1.2%, membranes with 96 vol% oil rejection were obtained. These membranes contained no crystals and exhibited strong bonds with the adhesive used for element preparation.

### Example 3

A vacuum gas oil distillate, having a viscosity of 4.93 cSt at 100°C, a refractive index of 1.4538 at 75°C, and a density of 0.8668 kg/dm<sup>3</sup> at 15°C, was countercurrently contacted in a commercial extraction tower with NMP containing 2.1% water. The tower bottoms temperature was 52°C.

A part of the extract solution, containing 9.7 wt.% oil was passed through a membrane unit, using an interfacially polymerized membrane of 1,4-phenylene diamine and trimesoyl chloride, operating at 93°C, which recovered a predominantly NMP permeate. The retentate of this unit, now containing 12.9 wt.% oil was equilibrated at the tower bottoms temperature of 52°C to produce a pseudo raffinate.

In a preferred mode of the invention, the equilibration settling drum and the membrane unit operate at the extraction tower bottoms temperature, which can be accomplished by lowering the membrane unit operating temperature, or by increasing the extraction tower temperature. The extraction tower temperature can be increased without affecting the product quality by lowering the solvent treat ratio and/or by increasing the solvent water content.

Material balance data around the extraction tower, the membrane unit and the settling drum indicated that 3.2 grams of pseudo raffinate solution was produced for every 100 grams of feed. Side by side extraction runs of distillate and a blended bead of distillate and pseudo raffinate in a countercurrent laboratory extraction unit are illustrated in the following table.

Table 2

	Base Case 1	Base Case 2	Recycle Case
Distillate feed, wt.	100	100	100
Pseudo raffinate, wt% on distillate	0	0	3.2
Raffinate RI	1.4538	1.4534	1.4536
Raffinate Density	0.8665	0.8658	0.8666
Solvent Treat (LV% on distillate)	186	194	190
Raffinate Yield (LV% on distillate)	80.8	79.6	83.5
Adjusted Raffinate Yield <sup>1</sup> (LV% on distillate)	80.5	80.4	83.3

<sup>1</sup>After correction to equal raffinate quality and 186% solvent treat

Results clearly illustrate the superior yield that is obtained by using the current invention.

Example 4

To determine preferred operating ranges for the invention, three primary extract solutions were prepared, with different oil concentrations. Subsequently, the NMP content of the solution was reduced, while the solution was maintained at the miscibility temperature of the base case, and the quantity and quality of the pseudo raffinate oil was measured. Results are shown in the following table.

Table 3Run A: Primary extract with 9.7% oil

## NMP Reduction

- removed by membrane	Base	-27%
Oil concentration	9.7	12.9
Pseudo Raffinate Yield,		
LV% on extract oil	--	13.8
Base Case Extract RI	1.5426	
Pseudo Raffinate RI @ 75 C	--	1.4651

Run B: Primary extract with 18% oil

NMP Reduction (simulated)	Base	-20%	-40%	-60%
Oil concentration	18	22	27	35
Pseudo Raffinate Yield,				
LV% on extract oil	--	8.1	12.6	19.3
Base Case Extract RI	1.5287			
Pseudo Raffinate RI @ 75 C	--	1.4678	1.4733	1.4821

Run C: Primary extract with 24% oil

NMP Reduction (simulated)	Base	-20%	-40%
Oil concentration	24	28	34
Pseudo Raffinate Yield,			
LV% on extract oil	--	0.7	0.8
Base Case Extract RI	1.5287		
Pseudo Raffinate RI @ 75 C	--	1.4813	1.4888

In Run A, NMP removal was accomplished by permeating part of the solution through a membrane, while in Run B and C, the membrane solvent removal was simulated by blending of extract oil and solvent in the appropriate proportions.

The table illustrates that solvent removal generates effectively a pseudo raffinate if the initial extract oil concentration is 10 and 18% oil, but is less effective if the initial oil concentration is 24%. It is expected that the invention will perform well with initial primary extract concentrations of less than 10% oil, but that the economic attractiveness of the primary extraction step would decrease because of the large quantities of solvent that would be required. Thus, the preferred primary extract oil concentration is between 5 and 25% oil in extract solution, and the most preferred oil concentration between 10 and 18% oil.

It is interesting to note that in Run B, solvent removal beyond the 24% oil concentration demonstrated in Run C remains effective in generating more pseudo raffinate, and that apparently the initial concentration of the oil is the main factor determining the quantity and quality of pseudo raffinate. However, at very high oil concentrations, the physical separation of the pseudo raffinate from the retentate in the settling vessel becomes more difficult, and the preferred oil concentration in the retentate of the membrane unit is between 10 and 35%, and most preferentially between 13 and 25%.

#### NOTES

- US patent application serial number 417333 filed 05.10.89 is equivalent to published European patent application EP-A-421676.
- US patent application serial number 434735 filed in November 1989 is published as US-A-4978454.

#### Claims

1. A method for the selective solvent extraction of aromatic hydrocarbons from mixtures of same with non-aromatic hydrocarbons in a hydrocarbon feed stream comprising contacting said hydrocarbon feed stream with a selective aromatic extraction solvent in a solvent extraction zone to produce an aromatics rich extract phase and an aromatics lean raffinate phase, passing the extract phase to a membrane separation unit and recovering a retentate, passing the retentate to a settling zone wherein the retentate spontaneously separates into two liquid phases, passing the upper phase back to the solvent extraction zone to thereby increase the yield of raffinate.
2. A variant of the method of claim 1 for the selective solvent extraction of aromatic hydrocarbons from mixtures of same with non-aromatic hydrocarbons in a hydrocarbon feed stream comprising contacting said hydrocarbon feed stream with a selective aromatics extraction solvent in a solvent extraction zone to produce an aromatics rich extract phase and an aromatics lean raffinate phase, and further comprising the step of passing a side stream comprising a mixed raffinate solution/extract solution which is taken from an intermediate zone of the solvent extraction zone and fed to a membrane separation unit whereby said mixed feed is separated into a solvent-raffinate rich permeate and an extract rich retentate and passing the extract rich retentate to a settling zone where it spontaneously separates into an oil rich pseudo raffinate upper phase which is recovered and into a solvent rich pseudo extract bottoms phase which is recycled to the solvent extraction zone at a point below that at which the side stream was withdrawn.
3. The method of claim 2 comprising passing the extract phase to a membrane separation unit and recovering a retentate, passing the retentate to a settling zone wherein the retentate spontaneously separates into two liquid phases, passing the upper phase back to the solvent extraction zone to thereby increase the yield of raffinate.
4. The method of any one of claims 1 to 3 wherein the membrane separation zone comprises an interfacially polymerized crosslinked membrane on microporous organic solvent resistant ultrafiltration backing, said interfacially polymerized membrane comprising the reaction product of a multi-functional amino compound dissolved in water with a polyfunctional agent dissolved in an organic solvent, at least one of which reactants is trifunctional, on a backing, and said contacting is under reverse osmosis conditions.
5. The method of claim 4 wherein the multifunctional amino group reactant is selected from polyethylenimine, polyvinylamine, polyvinylaniline, polybenzylamine, polyvinylimidazolines, amine modified polyepihalohydrines, m-phenylenediamine, p-phenylenediamine, triaminobenzine, piperazine, piperidine, 2,4-bis (2-amino-benzyl) aniline, cyclohexane diamine, cycloheptane diamine.
6. The method of claim 4 or claim 5 wherein the polyfunctional agent is selected from di- and tri- acid halides, acid anhydrides, aliphatic diisocyanates, aromatic diisocyanates, thioisocyanates, haloformates, sulfonylhalides and mixtures thereof.

7. The method of any one of claims 4 to 6 wherein the multi-functional amine compound in water is at a concentration in the range of from 0.1 to 10 wt.%, and the polyfunctional agent reactant in organic solvent is at a concentration in the range of from 0.1 to 5 wt.%.

5 8. The method of any one of claims 4 to 7 wherein the backing is selected from nylon, cellulose, polyester, teflon (polytetrafluoroethylene), polypropylene, polyethylene, polyethyleneterephthalate ultrafiltration membranes.

10 9. The method of any one of claims 4 to 8 wherein the ultrafiltration membrane support layer has pores in the range 0.02 to 0.1  $\mu\text{m}$ .

10. The method of any one of claims 1 to 9 wherein the aromatic rich extract phase contains from about 5 to about 25% oil, e.g., from about 10 to about 18% oil.

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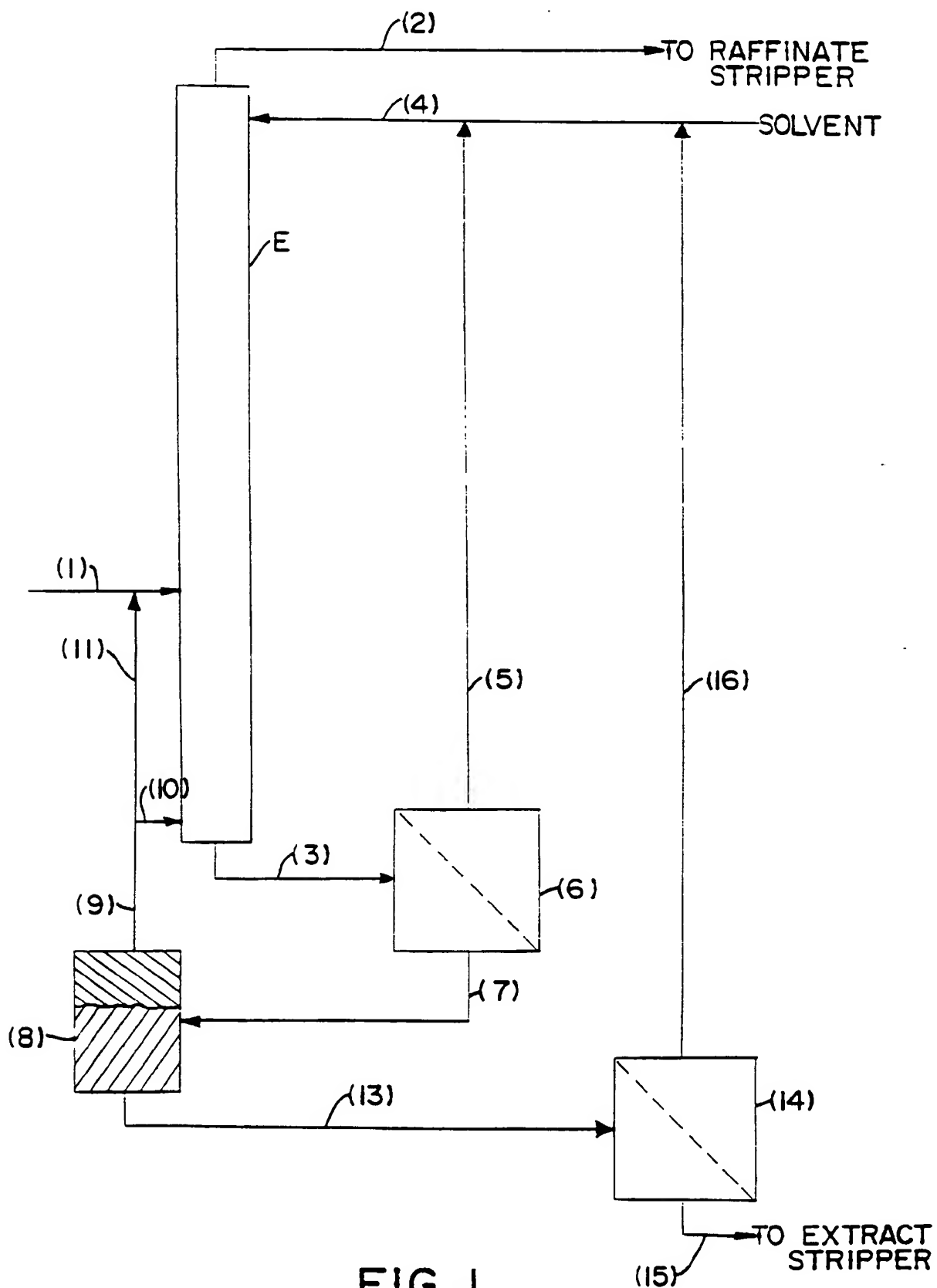
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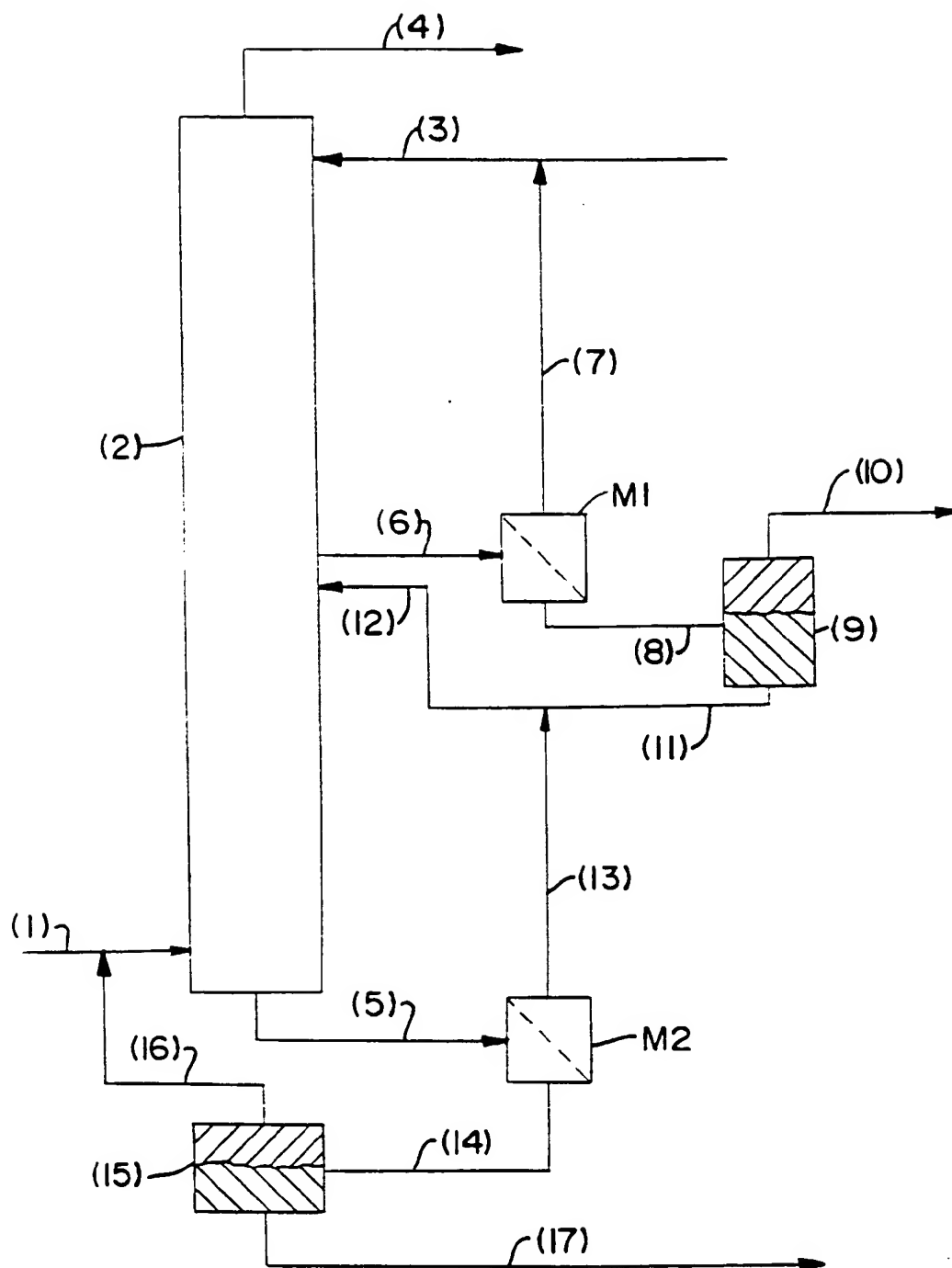


FIG. 2



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## EUROPEAN SEARCH REPORT

Application Number

EP 91 30 9458

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 145 126 (EXXON) * Page 1, lines 2-14; page 2, lines 1-8; page 12, lines 14-30; page 13, lines 1-17 * ---	1	C 10 G 31/11 C 10 G 21/00
A	EP-A-0 244 277 (INSTITUT FRANCAIS DU PETROLE) * Page 4, lines 40-49 * ---	1	
A	EP-A-0 217 534 (CANADIAN PATENTS) * Column 2, lines 6-25, 40-50; column 3, lines 7-45; column 4, lines 1-29 * ---	1	
X,P	EP-A-0 421 676 (EXXON) * Page 3, lines 33-52; page 4, lines 34-47 * -----	4,5,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G B 01 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-12-1991	Examiner KERRES P.M.G.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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